# Preparation and *X*-Ray Structure of a Novel Zwitterionic Organometallic Complex, $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$

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*Summary* The reaction between $[CuC_2C_6F_5]$ and $[ReCl(CO)_3(PPh_3)_2]$ affords $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$; an *X*-ray structure determination shows the complex to be a zwitterionic associate of $[Cu(PPh_3)]^+$ and $[Re(C_2C_6F_5)_2(CO)_3(PPh_3)]^-$ ions, in which Cu–acetylene $\pi$-bonding is present.

Reactions between substituted copper(I) arylacetylides and transition-metal complexes have recently afforded such interesting and novel structural types as $[FeCuCl(C_2Ph)(CO)_2(C_5H_5)]_2$,[1] $[RuCuCl(C_2Ph)(PPh_3)_2(C_5H_5)]$,[2] and $[Ir_2Cu_4(C_2Ph)_8(PPh_3)_2]$.[3]

Extending these studies to the Group VII elements, we have found that the reaction between *cis*-$[ReCl(CO)_3(PPh_3)_2]$ and $[CuC_2C_6F_5]$ yielded $[CuCl(PPh_3)]_4$, $[Re(C_2C_6F_5)(CO)_3(PPh_3)_2]$, and a copper-containing complex identified as $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$ by the usual methods, including mass spectrometry. The equivalence of both $C_6F_5$ groups was shown by the $^{19}F$ n.m.r. spectrum. The structure was determined by a single-crystal *X*-ray study.

*Crystal data:* $C_{55}H_{30}CuF_{10}O_3P_2Re$, $M = 1239{\cdot}5$, yellow triclinic crystals, $a = 15{\cdot}96$, $b = 13{\cdot}60$, $c = 11{\cdot}70$ Å, $\alpha = 84{\cdot}1°$, $\beta = 80{\cdot}6°$, $\gamma = 93{\cdot}0°$, $D_m = 1{\cdot}63$, $D_c = 1{\cdot}65$ g cm$^{-3}$ for $Z = 2$, space group $P\bar{1}$.

A total of 2683 visually estimated non-zero reflections (Mo-$K_\alpha$ radiation) was used in the structure determination. Standard heavy-atom procedures were followed, and the structure was refined using block-diagonal least-squares methods to the current conventional $R$ value of 7·7%.

The molecular structure is shown in the Figure, together with some relevant bond lengths. The two pentafluorophenylacetylide groups, the three CO groups, and the $PPh_3$ ligand occupy the six apices of an octahedron around the rhenium atom. The copper has approximate trigonal planar co-ordination, being attached to the second $PPh_3$ ligand, and asymmetrically to the two acetylide groups, as

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found in $[Ir_2Cu_4(C_2Ph)_8(PPh_3)_2]$.[3] The copper atom lies 0·11 Å out of the plane defined by the mid-points of the C–C triple bonds and the P atom. The Cu–P bond length, at 2·01(1) Å, is the shortest yet recorded {*cf.* 2·135 Å in $Cu(PPh_3)(C_5H_5)$;[4] 2·23(av.) Å in $[Cu(C_2Ph)(PMe_3)]_4$[5]}.

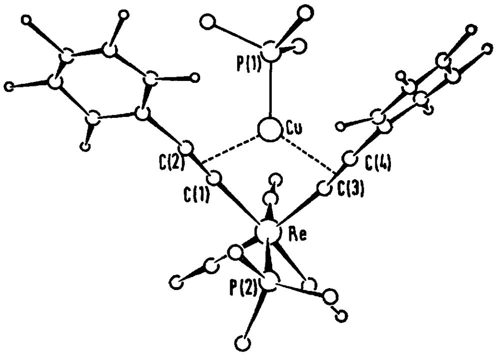

FIGURE. Molecular structure of $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$. The phenyl groups attached to the phosphorus atoms have been omitted for clarity. Bond lengths (Å), e.s.d. in parentheses: Re–Cu 3·078(3), Re–P(2) 2·19(1), Re–C(1) 2·39(2), Re–C(3) 2·26(2), Cu–P(1) 2·01(1), Cu–C(1) 1·98(2), Cu–C(2) 2·33(2), Cu–C(3) 2·12(2), Cu–C(4) 2·34(2).

The rhenium–acetylide bonds [2·26(2) and 2·39(2) Å] compare favourably with the estimated Re–C(*sp*) single bond length of 2·20 Å {*cf.* 2·242(av) Å in $[ReMe_2(C_5H_5)(C_5H_5Me)]$;[6] 2·32 Å in $[ReBrMe(CO)_2(C_5H_5)]$;[7] 2·22 Å in $[Re(COC_6H_4Cl\text{-}p)(CO)_5]$[8]}. The Re–P bond [at 2·19(1) Å] is shorter than those usually found {*cf.* 2·34 Å in $[ReH_3(dppe)_2]$[9]}.

The nature of the copper–rhenium interaction is of interest. The long Re–Cu distance [3·078(3) Å; estimated Re–Cu single bond, 2·81 Å] suggests that there is little, if any, direct metal–metal interaction. We suggest that the complex consists of ion-pairs $[Cu(PPh_3)]^+$ $[Re(C_2C_6F_5)_2(CO)_3(PPh_3)]^-$, additionally held together by the $\pi$-interaction between the copper and the acetylide groups. This interpretation, also supported by the normal octahedral (Re) and trigonal planar (Cu) geometries of the metal atoms, requires formal oxidation states of +1 for both metal atoms, rather than the unusual $Re^{II}$ and $Cu^0$ in the alternative model involving seven-co-ordinate rhenium and a metal–metal bond.

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